VISIT…

25
Refrigeration Lubes

Steven James Randles
ICI Wilton
Middlesbrough, Cleveland, England

I. HISTORY OF REFRIGERATION

Oliver Evans first proposed a closed cycle of refrigeration using volatile liquid in 1805. Jacob Perkin actually designed such a system and obtained a British patent in 1835. Jacob Perkin's vapor compression machine never advanced beyond the experimental stage, but his concept was developed into commercial use decades later. The earliest successful vapor compression system used ether. In 1869 ammonia (R717) refrigerants found their first successful commercial use. About the same time carbon dioxide (R744) was used commercially, followed by sulfur dioxide (R764) in the 1880s, methyl chloride (R40) in 1884, ethyl chloride (R160) in 1870, and isobutane in 1920 [1].

In the 1930s, scientists looking for a safe and effective refrigerant discovered a group of chemical compounds known as chlorofluorocarbons (CFCs). The CFCs were found to have a number of properties that made them ideal for use in refrigerants and for a number of other purposes. They proved so useful that until very recently, thousands of tons of CFCs were manufactured and used throughout the world.

A. The Move from CFC to HFC Refrigerants

Lately, the widespread use of CFCs has been associated with potentially damaging effects to the environment. The refrigerants are believed to damage the earth's protective ozone layer and to contribute to the so-called greenhouse effect. The harm that CFCs might actually cause was not really appreciated until the 1970s, about 40 years after they were first used. Since then serious efforts have been made to minimize the effects of CFCs.

At a meeting in Montreal in 1987, held under the auspices of the United Nations Environmental Program, some 27 countries signed an international agreement to control the production and use of CFCs and certain similar substances. The Montreal Protocol was revised and strengthened in London in June 1990 and in Copenhagen in November 1992. Further strengthening of the conditions in the agreement seems likely.

Once it was realized that CFC usage needed to be phased out, other chemicals had to be

Copyright © 1999 Marcel Dekker, Inc.

found to replace CFCs in essential applications. Many substances can be used as refrigerants. Most commonly used refrigerants are substances that can be changed easily from liquid to a gas and back again. These substances can be split into four main groups:

The so-called natural refrigerants such as carbon dioxide, propane, isobutane, and ammonia.
The chlorofluorocarbons (CFCs: e.g., R12), which contain only the elements chlorine, fluorine, and carbon.
The hydrochlorofluorocarbons (HCFCs: e.g., R22), which contain hydrogen in addition to chlorine, fluorine, and carbon.
The hydrofluorocarbons (HFCs: e.g., R134a, R407c), which contain hydrogen, fluorine, and carbon but no chlorine; the HFCs are the newest group of compounds.

Halocarbons that are used commercially are often denoted by the abbreviations such as CFC-, HCFC-, HFC-, R- (for refrigerant), or a trade name followed by a standard number designated by the American Society of Heating, Refrigeration and Air Conditioning Engineers (ASHRAE). The numbering system introduced by ASHRAE refers to the chemical structure of the refrigerant.

B. An Overview of a Basic Refrigeration System

Figure 1 shows a simple schematic of the basic components contained within a refrigeration system.

1. The Compressor

The refrigerant is drawn into the compressor and compressed into a smaller volume. Upon compression, the refrigerant molecules are squeezed together, causing their temperature and pressure to be increased. When the pressure of the refrigerant is increased, the boiling point also increases. The main purpose of the compressor is therefore to raise the pressure, temperature, and boiling point of the refrigerant above that of the surrounding air. Compressors for domestic appliances are in general hermetically sealed. They are housed in a welded can and are therefore

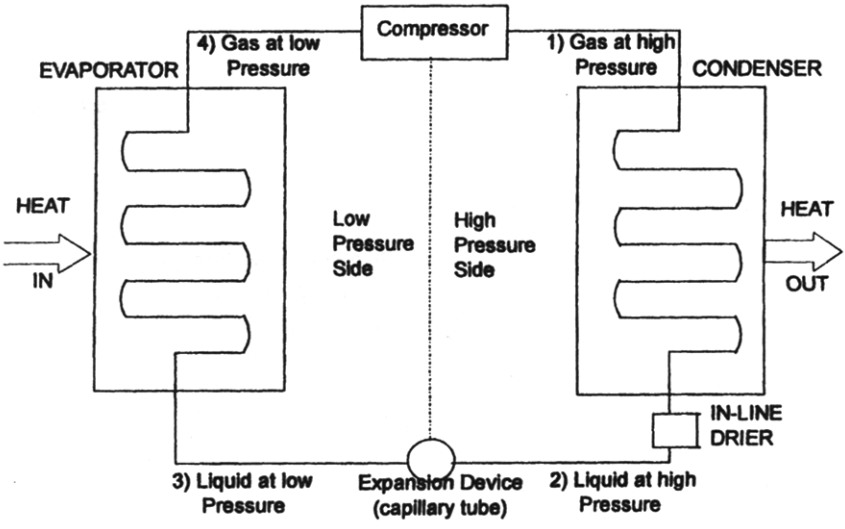


Figure 1 Schematic of a basic domestic appliance refrigerator.

Copyright © 1999 Marcel Dekker, Inc.

"sealed for life." Compressors for other application areas can be hermetic, semihermetic, or open, depending on the degree of access to the internal components of the compressor.

2. The Condenser

The refrigerant gas enters the condenser at relatively high temperature and pressure. The temperature of the refrigerant is reduced by the cooling medium (air for small units) until it begins to condense and form a liquid. This sequence involves a change in state, causing heat to be rejected. This explains why the back of a domestic refrigerator gets hot! Then refrigerant, under the influence of gravity, flows from the condenser as liquid at high pressure.

3. The Filter Drier

The refrigerant can then pass through an in-line filter drier. This device removes contamination (water, acid, wear debris) from the refrigerant liquid before it reaches the expansion device. Filter driers are typically either molecular sieve, activated alumina, or combinations of these types.

4. The Expansion Device

The refrigerant enters the expansion device as a liquid at high pressure. The function of the expansion device is to regulate the flow of the liquid refrigerant into the evaporator, thereby reducing the pressure.

The most common type of expansion device is a capillary tube, which basically consists of a narrow bore copper tube. Capillary tube restrictions operate on the principle that liquid passes through them much more rapidly than vapor, which makes them a practical device for controlling refrigerant flow. To avoid any blockage in the capillary tube, system cleanliness must be achieved and maintained. A second type of expansion device is the thermal expansion valve (TXV). The refrigerant leaves the expansion device and enters the evaporator as a low pressure liquid. Capillary-based expansion devices are used in domestic appliance application, while TXVs are favored in the industrial commercial sector.

5. The Evaporator

There are two main types of evaporator. In dry evaporators, vapor occupies a considerable part of the volume. In flooded evaporators, the refrigerant space is largely filled with liquid. Flooded evaporators provide more rapid cooling, because the rate of heat transfer to liquid refrigerant is higher than the rate of heat transfer to refrigerant vapor.

Liquid refrigerant enters the evaporator at a pressure that permits it to boil readily. This involves a change in state, and heat is absorbed (latent heat of evaporation); hence it is cold inside the refrigerator. As the refrigerant passes through the evaporator, heat flows into it so that the boiling process continues. When the refrigerant reaches the outlet of the evaporator, it has completely vaporized and becomes a gas. Typically, to ensure that no liquid reaches the compressor, the refrigerant is slightly superheated and the pipe to the compressor is lagged. The refrigerant now enters the compressor as gas at low pressure and the refrigeration cycle begins again.

II. DESIRABLE PROPERTIES OF REFRIGERATION LUBRICANTS

Refrigeration lubricants should:

Act as an oil seal (at pistons, valves, gland seal, etc.) for compressed gas between suction and discharge sides in a compressor.
Act as a coolant to remove heat from the crankcase to the compressor exterior.

Copyright © 1999 Marcel Dekker, Inc.

Reduce noise generated by moving parts in the compressor.
Lubricate internal parts.

Desirable properties of a refrigeration lubricant include the following [2]:

It should have good lubricity and be able to provide good energy efficiency.
It should be chemically stable.
It should have low hygroscopicity (low water uptake).
It should have high thermal conductivity (good coolant).
It should have good electrical resistivity and breakdown voltages (for compressors with internal switches).
It should be environmentally acceptable (no handling problems).
It should be compatible with materials of construction of the compressor. It should be soluble with the refrigeration gas, mineral oil, and additives (no transport or heat transfer problems).

III. HISTORICAL DEVELOPMENT

A. Earlier Uses of Synthetics in Refrigeration Application

The first use of synthetic lubricants dates back to 1929, when the first synthetic oil manufactured was thought to be of use in ice-making equipment. Fifteen years later polyalkylene glycols (PAGs) were considered for the same application. The mid-1950s saw the introduction of alkyl-benzenes [3]. Polyol esters were used with R22 systems, with evaporator systems of 280°C, in the late 1960s [4].

The limited solubility of mineral oils with R502 and R13 initially led to the first in-depth investigation of synthetic oils for refrigeration use. One result was the finding that alkylbenzenes give satisfactory performance in these systems [2]. Sanvordenker and Larime [3] were among the first to characterize the suitability of a wide range of synthetics (diesters, polyols, PAGs, phosphate esters, and alkylbenzenes) for use with R22 and R502. Until recently, however, the use of synthetic lubricants was limited for reasons of cost.

B. The Need for Synthetics

In the past, compressors in refrigeration systems were lubricated with mineral oils. Systems that use HFCs, such as R134a, however, cannot be lubricated with mineral oil, mainly because of its poor solubility with HFCs. Poor solubility can give rise to several potential problems, namely:

Formation of liquid plugs inside the condenser, causing the system to splutter as they pass through the expansion device;
Buildup of oil on the evaporator walls, leading to reduced heat transfer and poorer energy efficiency;
Poor oil transport, resulting in the compressor being starved of oil.

Solubility issues are also causing a move from mineral oil to synthetics in applications that use refrigerants of other types, such as ammonia and carbon dioxide.

IV. TYPES OF SYNTHETIC LUBRICANT USED

Table 1 lists refrigerants and possible lubricants that can be used.

Mineral oil lubricants have poor solubility with ammonia. This is a benefit in flooded evaporator systems, since these oils are heavier and can be easily removed (by draining from the

Copyright © 1999 Marcel Dekker, Inc.

Table 1 Some Refrigerant–Lubricant Combinations

Alternative refrigerant	Suitable lubricants
Chlorofluorocarbons (CFCs: e.g., R12)	Mineral oil
Hydrofluorochloro-Carbons (HCFCs: e.g., R22)	Mineral oil Alkylbenzenes Polyol esters
Hydrofluorocarbons (HCFs: e.g., R134a, R407C)	
Industrial, commercial	Polyolesters
Automotive air conditioning	Polyalkylene glycols
Ammonia	Mineral oil poly (α – olefins)
Conventional	Alkylbenzenes
Dry/direct evaporation	Polyalkylene glycols
Hydrocarbons (e.g., propane, R290; isobutane, R600a)	Mineral oil Esters, Polylalkylene Glycols
Carbon dioxide	Esters, Polylalkylene glycols

bottom of the evaporator vessels) and returned to the compressor [5]. However, the poor solubility limits the use of mineral oil with systems that employ direct exchange evaporators. Here, the immiscible oil builds up in the evaporator, reducing its efficiency and ultimately leading to oil starvation. This set of problems can be prevented by the installation of an oil separator, but this results in additional materials costs, a larger system, and an increase in the amount of servicing the compressor requires. Polyalkylene glycols can be optimized to be soluble with ammonia. This property has allowed them to be used in refrigerators with direct expansion evaporators. Esters are not used because they can react with ammonia, leading to the formation of deposits.

Polyalkylene glycols also offer advantages over mineral oil when used with hydrocarbon refrigerants as, even at high pressure, they resist dilution by the gas and thus provide improved compression efficiency. Esters are also being evaluated because of their environmental benefits (e.g., biodegradability, renewable resource).

The refrigerants of choice to replace CFCs are the HFCs. Much of the early work on lubricants for HFCs focused on polyalkylene glycols. However, they were found to have several major drawbacks, namely:

Hygroscopicity leading to absorption of between 3000 and 25,000 ppm of water, depending on structure;
Poor dielectric breakdown voltages (related to high moisture contents);
Copper plating (due in part to high water content);
Poor miscibility/solubility with minerals, leading to potential retrofit problems;
Poor suitability as lubricants for aluminum contacts;
Poor materials compatibility.

In automotive air conditioning applications many of the issues above either were not relevant or could be engineered around. PAGs are therefore the current lubricant of choice for this application. Most of the PAGs are doubled end-capped to improve thermal stability, reduce hygroscopicity, increase mineral oil miscibility, and increase lubricity. Because PAGs have poor solu-

Copyright © 1999 Marcel Dekker, Inc.

bility with mineral oil, however, polyol ester tend to be used as the oil of choice for retrofit market.

For domestic appliance and industrial/commercial applications, polyols esters (POEs) have become the lubricant of choice. The reasons for POE adoption in these areas are described in detail later in this chapter.

For carbon dioxide refrigerants, esters have gained some acceptance. As pressure changes, the density of the carbon dioxide varies. This can lead to "phase inversion." That is, the lubricant sometimes floats on the surface of liquid carbon dioxide and sometimes sinks, depending on pressure. This makes the separation of lubricant from the refrigerant very difficult [6]. Esters, because of their high miscibility, provide a method of avoiding this situation. Carbon dioxide is currently being evaluated as a possible refrigerant by several German automotive original equipment manufacturers (OEMs).

Esters, PAGs, and alkylbenzenes are covered in greater depth in Chapters 3, 6, and 7 of this book.

V. OPTIMIZING THE PERFORMANCE CHARACTERISTICS OF POES

A. POEs Versus Mineral Oil

Pentaerythritol polyol esters comprise the main type of POE used in refrigeration applications. A schematic of such an ester is shown in Fig. 2.

HFC refrigerants are very polar. An old rule of thumb that is often used by chemists is "like dissolves like." In short, polar lubricants are soluble in polar refrigerants. The ester linkages in polyol esters make the lubricant very polar. It is mis polarity that makes the ester soluble in HFC and HCFC refrigerants (see below-Section V.B.I).

The polarity of the ester, however, has several other side effects, namely:

Conventional processing oils have a high solubility in the ester. This can lead to several problems (see Section V.B. 3).

Being polar, the HFC refrigerants stick to steel surfaces better, making them better boundary lubricants than mineral oil. POEs have much higher loads-to-fail than their mineral oil equivalents.

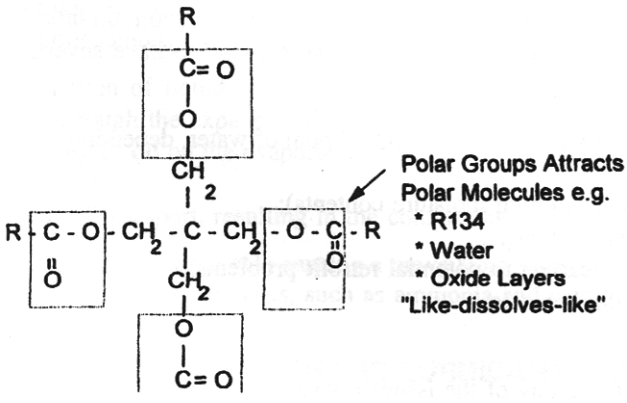


Figure 2 Schematic of a pentaerythritol polyol ester.

Copyright © 1999 Marcel Dekker, Inc.

Foaming characteristics must be dealt with (see Section V.B. 4).

Water is a polar molecule and tends to be attracted to the ester linkage. This means that HFC-soluble lubricants such as POEs and PAGs are more hygroscopic than their mineral oil equivalents. This is illustrated in Fig. 3.

Polyol esters have a maximum water uptake of between 1000 and 2500 ppm of water, depending on chemistry, temperature, and relative humidity. Modified PAGs (end-capped) have much lower water uptakes than unmodified PAGs and therefore tend to be the lubricant of choice in the automotive sector.

B. Types of POE

Neopentyl polyol esters are made by reacting a polyhydric alcohol and a monobasic acid under conditions of elevated temperature and pressure to form an ester and water. The ester is neutralized to a low total acid number (TAN): typically less than 0.04 mg of potassium hydroxide per gram. The structures of the typical types of neopentyl polyol alcohol used in the refrigeration lubricants area are given in Fig. 4.

There are three main ways of modifying the performance of polyol esters and are as follows:

changes in chemistry
boosting purity (e.g., by means of tight manufacturing levels of water, acid, degree of reaction, etc.)
formulation with additives.

The chemistry of the polyol ester can be altered by changing the following:

the type of alcohol used: dipentaerythritol (DiPE), pentaerythritol (PE), trimethyol propane (TMP), or neopentyl glycol (NPG)
the molecular weight of the acid
the degree of branching of the acid.

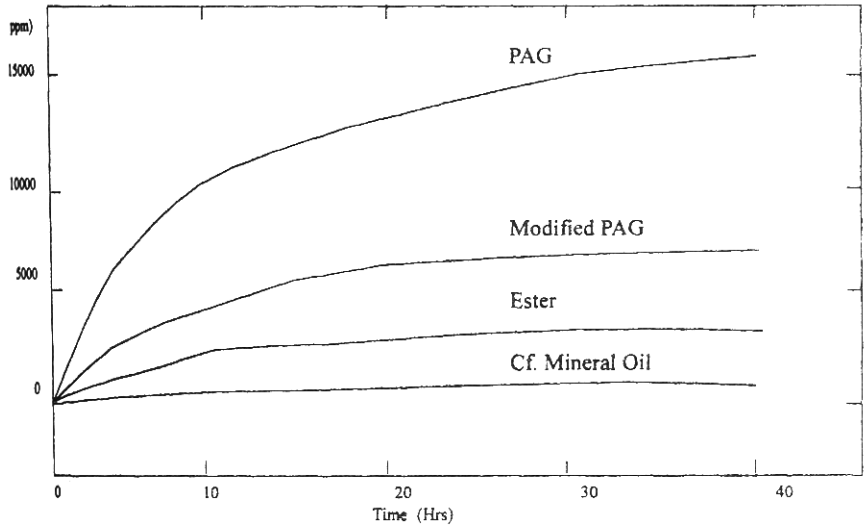


Figure 3 Plot showing the hygroscopicity of PAG and POE lubricants.

Copyright © 1999 Marcel Dekker, Inc.

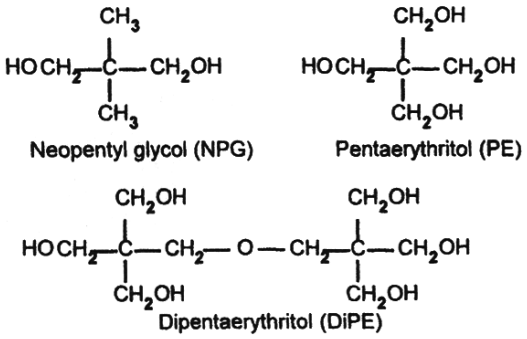


Figure 4 Schematic of alcohols used in refrigeration lubricants.

Figure 5 gives typical examples of the acids used in refrigeration lubricants. The chain length of the acids will typically range from five to ten carbons. Acids with chain lengths smaller than five carbon atoms give concerns relating to their high corrosiveness, while very long chains (. 10 C) can lead to solubility problems and poor low temperature flow properties, which in turn can lead to oil transport difficulties.

1. Optimizing the Structure of Polyol Esters

The viscosity of POE lubricants is related to their molecular weight, which is influenced by the selection of the polyfunctional alcohol.

Typically, blends of NPG with PE are used for low viscosity esters (, ISO 22) and PE with diPE for the higher viscosities (. ISO 46). These alcohols are then reacted with a range of acids, which have a major impact on the performance of the ester.

Two main types of ester are used commercially, these are:

HSPOEs (hindered structure polyol esters) based on completely branched acid esters (e.g., 2-ethylhexanoic acid, 3,5,5-trimethylhexanoic acid).

HOPOEs (highly optimized polyol esters) based on a mixture of linear and branched esters. For low viscosity esters (, ISO 22), these are based on wholly linear acids.

Table 2 shows me trade-off in properties obtained from using either linear or branched acids.

Early studies [7,8] suggested that chlorinated refrigerants played a significant role in improving the antiwear performance of mineral oil. This was due to a contribution to boundary lubrication. For example, R12 reacts with steel surfaces to form a protective film. The high

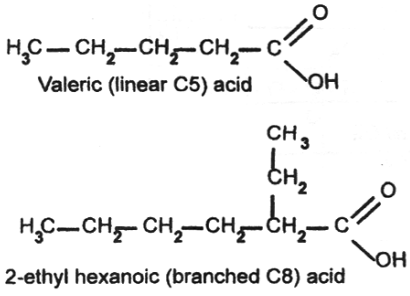


Figure 5 Schematic of acids typically used in refrigeration lubricants.

Copyright © 1999 Marcel Dekker, Inc.

Table 2 Positive (+) and Negative (-) Trade-offs from Using Linear or Branched Acids

Parameter/Property	Molecular weight[a]	Polarity[b]	Branching[c]	Structural diversity[d]
Lubricity	+	+	–	
Viscosity	+		+	
Viscosity index	+		–	
Pressure viscosity coefficient	+		+	+
Thermal stability	–		–	
Hydrolytic stability		–	+	
Pour point	–			+
Miscibility	–	+	+	+

[a] Increasing chain size.
[b] Number of ester linkages and size of ester.
[c] Increased degree of branching.
[d] Number of different acids used.

temperatures and contact pressures developed under the conditions of metal-to-metal contact cause the refrigerant molecule to decompose, resulting in the formation of active chlorine products that react chemically with metal surfaces to form protective chlorine boundary layers. Refrigerants with high levels of chlorine (e.g., R12) have been found to be particularly effective. HFC refrigerants do not contain any chlorine and therefore contribute little to antiwear behavior. Lubricants for use with HFC refrigerants, therefore, have to be greatly superior in lubricity than their mineral oil equivalents.

Linear acid HOPOE lubricate better than their branched HSPOE equivalents. This can be seen in Fig. 6, which plots the results of a Falex test run under an R134a atmosphere, 200 lb, steel/aluminum contacts. Linear acid based HOPOE also tend to have frictional properties superior to those of their branched equivalents (Table 3). Friction coefficients were measured using the IP 24ID Falex test. Detailed reasons for the superiority as lubricants of linear acid esters over their branched acid equivalents are given in Section III.2.3 of Chapter 3.

Branched acids are better at increasing viscosity than linear acids. They therefore tend to be incorporated in lubricants of higher viscosity. The readily available 3,5,5-trimethylhexanoic acid has particularly good thickening capability and is commonly used. As shown in Table 4, however, linear acid based esters tend to have viscosity indices superior to those of their branched equivalents.

HSPOE lubricants tend to have better hydrolytic stability. The hydrolytic stability of an ester is chiefly dependent on the amount of water in the system. Figure 7 illustrates that branched esters hydrolyze more slowly than linear esters but will equilibrate to the same acid value [9]. This final acid value, TAN, is dependent on the initial water content in the system, not on the type of POE.

The hydrolytic and thermal stabilities of POEs are covered in more detail below, in Section V.B.3, and in Chapter 3 of this book.

There have been problems with the pour point of HSPOEs; these issues are covered in more detail later (see Section V.B.3). We move shortly to me miscibility of linear versus branched acid ester (Section V.B.2).

Copyright © 1999 Marcel Dekker, Inc.

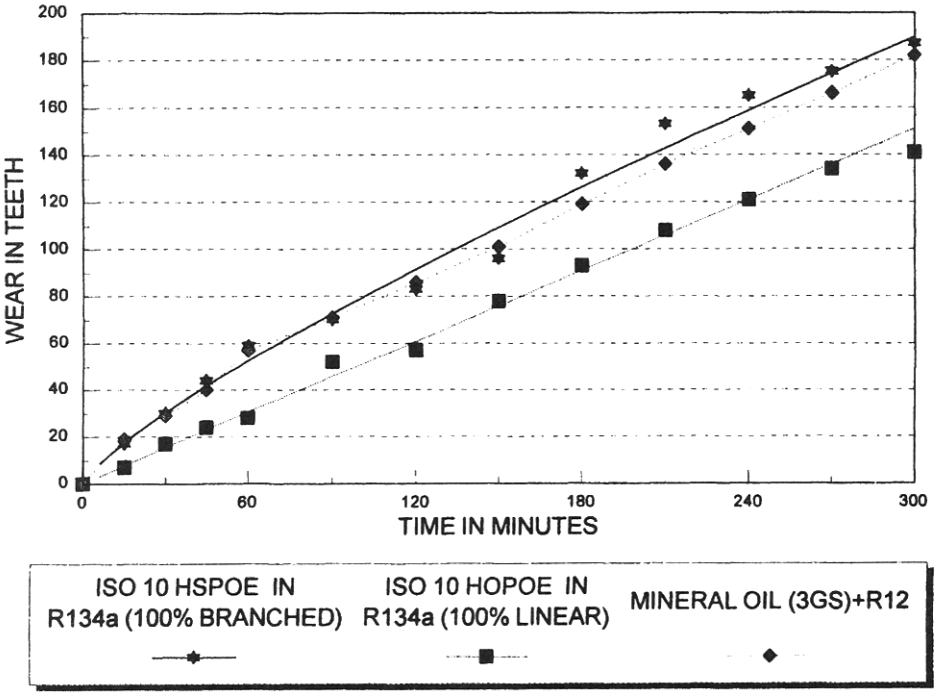


Figure 6 Results of a Falex wear test of R134a for a wholly linear (HOPOE) and a wholly branched (HSPOE) acid lubricant, viscosity ISO 10.

Table 3 Frictional Properties of POEs

	HOPOE		HSPOE	
ISO grade	Friction coefficient	Comments	Friction coefficient	Comments
15	0.07	Light wear	0.10	Severe wear
22	0.06	No wear	0.08	Light wear

Table 4 Comparison of Viscosity Indices (ISO) for HOPOEs and HSPOEs

ISO grade	HOPOEs	HSPOEs
7	144	90
10	112	57
15	115	50
22	128	73

Copyright © 1999 Marcel Dekker, Inc.

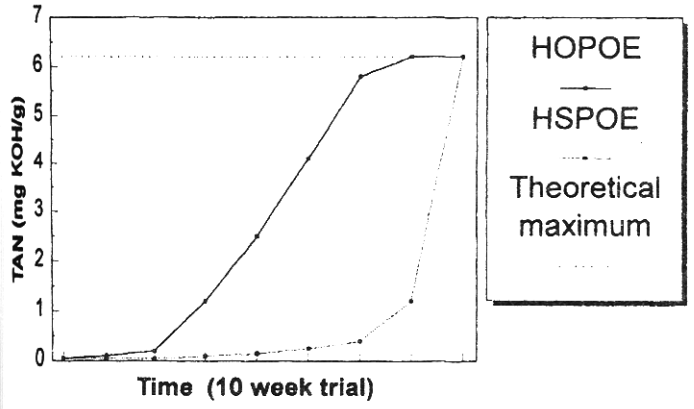


Figure 7 Hydrolysis of linear versus branched polyol esters: TAN, total acid number (2000 ppm initial moisture; 150°C). (From Ref. 9.)

Generally, HSPOEs offer a combination of good miscibility and hydrolytic stability at the expense of lubricity and thermal stability. Many HSPOEs therefore require formulation with an antiwear additive to avoid wear problems. However, antiwear additives have been found to give many problems in the field, and this area is covered in more detail later in the chapter.

HOPOEs offer excellent wear performance, low wear, and high thermal stability combined with acceptable performance in hydrolytic stability and miscibility. Field trials and subsequent extensive industrial usage established HOPOEs as a commercially important class of POEs.

2. Optimizing Solubility and Miscibility of POEs

Refrigerants and lubricants are classified as completely miscible, partially miscible, or immiscible, according to their mutual solubilities. Mutual solubility is defined as the capability of either phase (liquid and/or gas) to dissolve the other.

Completely miscible refrigerants are mutually soluble in all proportions at any temperature.

Partially miscible refrigerants are mutually soluble to a limited extent. Above the critical solution temperature (CST), oil–refrigerant mixtures in mis class are completely miscible and their behavior is identical to that described above. Below this temperature the liquid may separate into two phases. Such phase separation does not mean that the oil and the refrigerant are insoluble in each other. Each liquid phase is a solution, one is oil-rich and the other refrigerant-rich, depending on the predominant component. Each phase may contain substantial amounts of the minor component, although the two solutions themselves are immiscible (Fig. 8).

Figure 9 gives a typical example of a miscibility curve for a polyol ester. The two critical solution temperatures are called the lower critical solution temperature (LCST) and upper critical solution temperature (UCST). The lower critical solution temperature is so named because it lies below a two-phase region, even though it occurs at a higher temperature than the UCST. This situation is unusual in small molecule mixtures, but it is the normal behavior in polymer solutions. Such behavior has been explained by means of enthalpy and entropy of dilution theory and the use of free volume concepts.

Historically, mineral oils refined from naphthenic fluids have been used for refrigeration. These oils were highly dewaxed to remove refrigerant insolubles and refined further to improve chemical stability with CFC refrigerants. Therefore, past users had become accustomed to complete miscibility between R12 and mineral oil and assumed that total miscibility was a necessity. The main reason cited was poor oil return to the compressor from the evaporator (the evaporator

Copyright © 1999 Marcel Dekker, Inc.

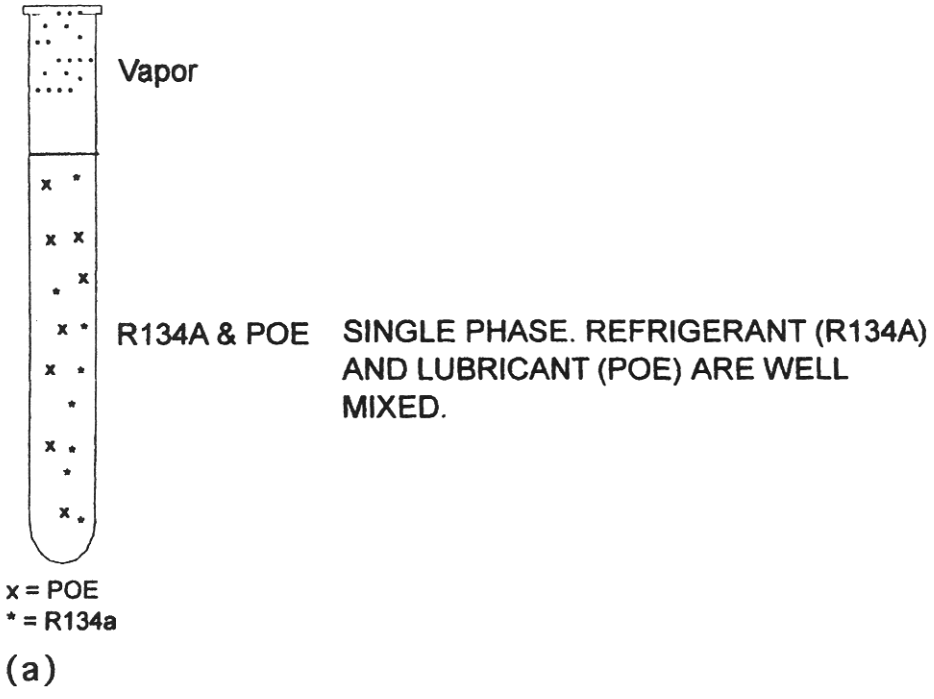


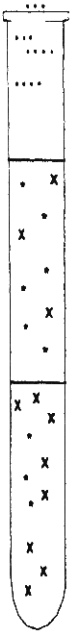
Figure 8 Three schematic depictions of the differences between miscibility and solubility: (a) miscible and soluble; (b) immiscible but soluble; and (c) immiscible and insoluble.

is the coldest part of the system, and the part of the system in which phase separation is most likely to occur). In dry-type evaporators for soluble/immiscible oils there is usually enough turbulence to cause the phases to emulsify. Flooded evaporators are more problematic. The excellent low temperature flow properties of synthetic oils can also reduce the problem of oil return. In practice, thousands of supermarket installations showed no problems of oil return even though the refrigerant (R502) showed some immiscibility with the mineral oil lubricant [10]. Another reason cited was the possibility that the phase-separated lubricant would coat the evaporator walls, causing low heat transfer. A reduction in heat transfer would manifest itself as a reduction in energy efficiency. Experiments have shown that the concentration of lubricant in the refrigerant phase is below 1% over the majority of the evaporation process and that excellent lubricant miscibility does not appear to be a significant lubricant factor. Good miscibility is desirable, but complete miscibility is not a necessity.

Several theoretical and semiempirical relationships are useful in correlating the solubility of a liquid in a compressed gas with various properties of the lubricant and the gas. Some of these correlations are of use in predicting the solubility of gas in a nonpolar liquid.

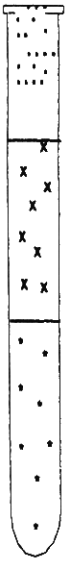
In its simplest form, regular solution theory, developed by Hilderbrand and coworkers [11], allows a correlation of gas solubility with the differences in solubility parameter between the liquid and the gas. "Solubility parameter" is defined as the square root of the cohesive energy density; that is, it is a measure of the strength of the intermolecular cohesion in the refrigerant or lubricant. As the difference approaches zero, solubility increases, in line with the old adage, "like dissolves like." By itself, the solubility parameter can explain the behavior of only a relatively small group of lubricants, those with little or no polarity and with weak or no hydrogen bonding. To extend its use to polar materials such as esters and fluorocarbons, it is necessary

Copyright © 1999 Marcel Dekker, Inc.



TWO DISTINCT PHASES ARE SEEN. HOWEVER, SOME POE IS PRESENT IN THE REFRIGERANT (R134A) PHASE AND SOME R134A IS PRESENT IN THE LUBRICANT (POE) PHASE.

(b)



TWO DISTINCT PHASES WITH NO INTERMIXING BETWEEN THE LUBRICANT (MINERAL OIL) AND THE REFRIGERANT (R134A).

x = Mineral Oil
* = R134a

(c)

Copyright © 1999 Marcel Dekker, Inc.

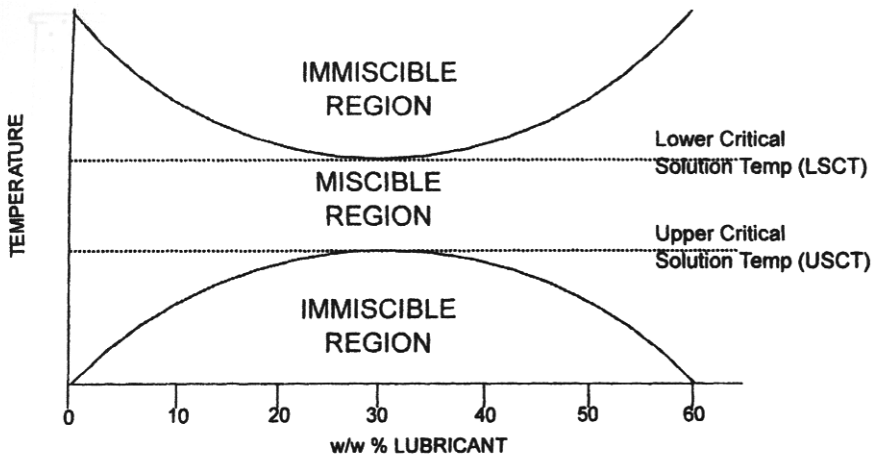


Figure 9 Miscibility curve for a typical POE lubricant.

to consider more specific forces and interactions. To this end, Hansen [12] developed the concept of three-dimensional solubility parameters of the form:

$$\delta(t)^2 = \delta(d)^2 + \delta(p)^2 + \delta(h)^2$$

where δt 5 total cohesion parameter
δd 5 dispersion cohesion parameter
δp 5 polar cohesion parameter
δh 5 hydrogen-bonding cohesion parameter

Values for these parameters for a wide range of solvents, lubricants, and refrigerants have been compiled by Barton [13]. In some applications only two of the three Hansen parameters are used, with the result that the locations of the liquids may be displayed on two-dimensional maps. For refrigeration gases Barton found that δp and δh were particularly useful, and such a graph is displayed in Fig. 10. Inoue and Iwamoto [14] derived values for δt, δd, δp, and δh for R134a of 13.9, 7.2, 7.4, and 9.5 $MPa^{0.5}$, respectively.

Figure 10 illustrates that nonpolar hydrocarbon oils such as mineral oil or alkylbenzenes have poor solubility, while polar oils such as polyalkylene glycols and esters have better solubilities (solubility being indicated by overlapping regions).

The use of solubility parameters to predict the solubility of a specific ester in a refrigerant is limited by the amount of experimental work required to calculate δp and δh of each ester. In fact, it is easier to measure the solubility of the ester directly. Also solubility parameters, even three-dimensional ones, tend to be less reliable, the greater the polarity. Solubility parameters are therefore useful to indicate which classes of lubricants are soluble with a refrigerant, but more tailored models are required to predict solubilities of specific esters. They do however indicate the importance of inter- and intramolecular forces (i.e., polar lubricants dissolve polar refrigerants).

Solubility parameters have been used extensively to predict the effect of a range of fluids on elastomeric seals. Van der Waal [15] used the concept of nonpolarity index (NPI) to predict the seal-swelling properties of esters. Nonpolarity index can be used as a simple method of estimating the polarity of an ester, and it gives a good indication of the inter- and intramolecular forces. It is calculated in the following way:

Copyright © 1999 Marcel Dekker, Inc.

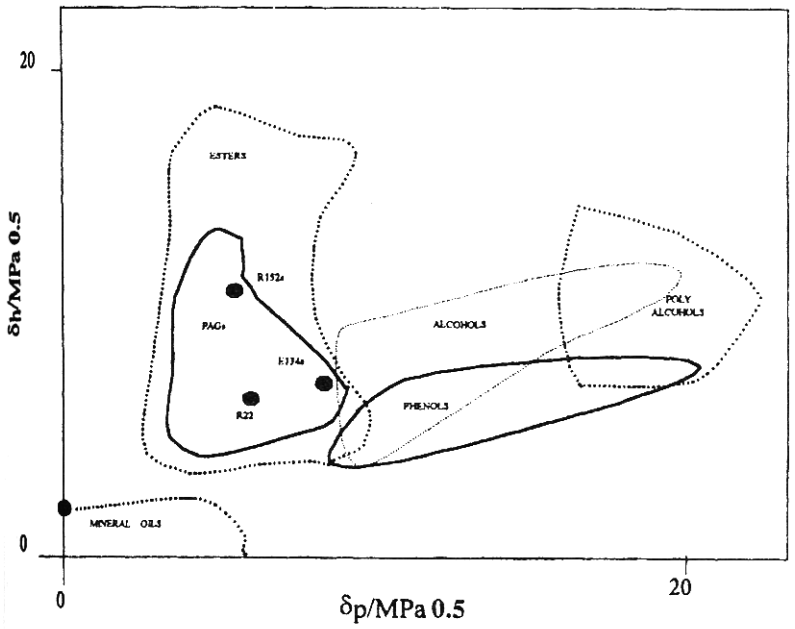


Figure 10 The effect of the solubility parameter on refrigerant–lubricant solubility.

$$\text{NPI} = \frac{\text{total number of C atoms} \times \text{molecular weight}}{\text{number of carboxylate groups} \times 100}$$

Figure 11 shows that a general trend can be seen when the NPI of the ester is plotted against the UCST for 10% lubricant in R134a.

Branching of the acid chain can influence the inter- and intramolecular forces in two main ways:

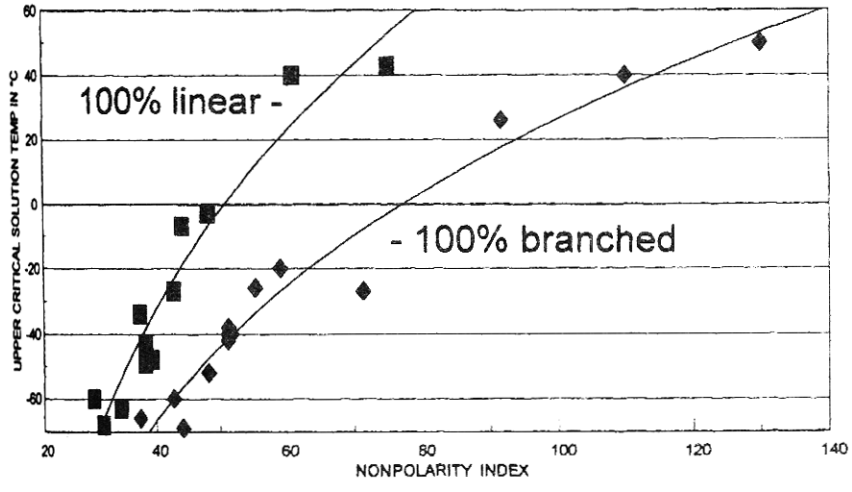


Figure 11 NPI versus UCST for a range of linear and branched POEs.

Copyright © 1999 Marcel Dekker, Inc.

Branched acid groups occupy a smaller molar volume. This means that for a branched acid ester of a given molecular weight, the polarity is spread over a smaller area than that of a similar linear ester of the same molecular weight.

Because of the smaller size of the acid arm, the polar refrigerant gas can approach the polar ester linkage more closely.

The molecular weight and branching of an ester are also related to viscosity, which means that branched acid esters are more miscible than the linear ones for a given viscosity.

The degree of solubility of the refrigerant in the lubricant is a very important performance criterion. The viscosity of lubricants at a given pressure, as exemplified in Fig. 12, can be markedly affected by the presence of dissolved refrigerant. For instance, R22 has a higher solubility in esters than in mineral oil. This usually means that an ester one ISO grade higher than the current viscosity mineral oil needs to be used to give an equivalent working viscosity. These data are known as vapor—liquid equilibria (VLE) measurements, and they are vital to ensure that the correct lubricant viscosity is used.

Data collected by bearing manufacturers has shown that the pressure-viscosity coefficient can be affected by refrigerant concentration and this relationship is not always linear [16]. Marked drops in viscosity-pressure coefficient are seen if the refrigerant concentration is higher then 20%. This can be counterintuitive. If the bearing temperature increases, the amount of dissolved refrigerant in the lubricant is likely to be reduced. This means that a given lubricant may actually have a higher viscosity at a hotter bearing than it would have at a cooler bearing.

3. Deposit Formation

It is well known that deposits, such as valve coking, have the potential to cause various problems in a compressor, leading to reduced long-term reliability. Since the coldest point in most refrigeration systems is at the exit of the expansion device into the evaporator, materials that have low solubility in the refrigerant–lubricant mixture will tend to precipitate at this point. Such deposition can result in flow restriction through the capillary tube or expansion valve orifice with materials of relatively high pour points such as waxes and gums, leading to a reduction in system performance, poor temperature control and, in extreme cases, system failure.

Deposits or accumulation of insoluble materials can also be found in other system compo-

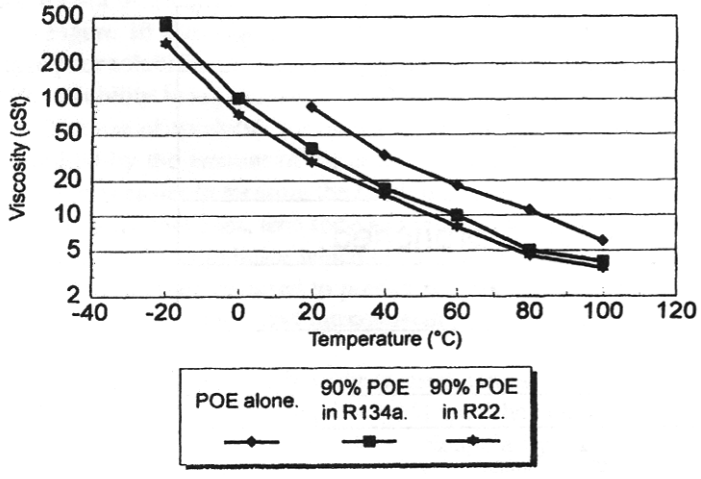


Figure 12 The effect of dissolved refrigerant on viscosity.

Copyright © 1999 Marcel Dekker, Inc.

nents—in particular in the evaporator. With sufficient material present, this can result in a reduction in heat transfer and a consequential drop in energy efficiency.

Given the relatively small quantity of material required to influence the expansion device, this chapter focuses on factors influencing deposit formation in capillary tubes and expansion valves.

Mechanism of Deposit Formation. There are a variety of mechanisms for the formation of deposits in (compressors and associated) refrigeration systems. These are summarized in Fig. 13 [17].

System Extractables. There are several possible sources of system extractables. These include the following:

Process chemicals used in the production and assembly of compressors and compressor components (e.g., assembly fluids, wire winding lubricants, detergents, corrosion inhibitors, fluxes).
Extractables from the nonmetallic *components* used in me construction of the compressor (e.g., elastomers, plastics, insulating material for slot liners and wires, varnishes for motor windings, tying cords).
lubricant components (e.g., additives, poorly soluble lubricant basestock components).
Inorganic components (e.g., machining debris, desiccant fines, copper plating).

The mechanisms of deposition of material from each of the different sources are complex. An overview of the main mechanisms is set out next.

Process Chemicals. The majority of the conventionally used process chemicals differ in solubility—in most cases being lower—in HFCs compared to CFCs and HCFCs. Particular problems have been observed with low pour point paraffinic processing oils such as wire winding lubricants and assembly oils. In many hermetic systems the copper motor windings are immersed to some extent in a lubricant-rich fluid at elevated temperatures (. 60°C). The conventional paraffinic wire winding lubricants are soluble in esters at the low HFC levels encountered under low pressure compressor sump conditions. It is well established that a small amount of lubricant is transported out of the compressor and into the system. It is therefore inevitable that the paraffinic wax dissolved in the ester-refrigerant mixture will pass through the expansion device. The envi-

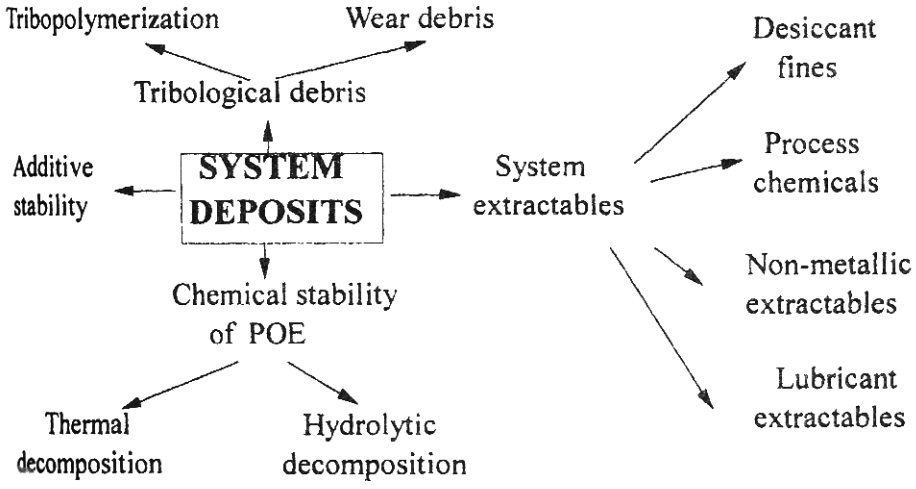


Figure 13 Schematic of mechanisms for deposit formation.

Copyright © 1999 Marcel Dekker, Inc.

ronment in the region of the expansion device is quite different from that encountered in the compressor sump—namely, it is rich in refrigerant (. 98%) and low in temperature.

The poor solubility of the paraffinic material under these conditions causes it to deposit in the expansion device, as illustrated in Fig. 14.

The waxy surface of the paraffinic material deposited in the expansion device tends to entrap further system debris, causing further deposit buildup. This results in a heterogeneous deposit made up of many different phases. Given the relatively small amounts of material necessary to impair system performance coupled with the compositional complexity of the deposits, a high degree of sophistication in analytical chemistry is necessary to understand the root cause of the problem. This is discussed in further detail below.

Studies on field systems show that such deposits often have the appearance of a white waxy grease with included debris. Extensive field testing has shown that this material can build up rapidly, in some instances after only hours of running, and it usually reaches saturation levels after several weeks of running. In industrial systems it is often possible to clean deposits from a TXV. Following a retrofit, any such deposited material can be removed by cleaning and, unless the system is heavily contaminated, is not likely to recur. In contrast, capillary tube systems cannot easily be cleaned, and it is therefore important to address the issue at source—that is, by controlling the level and type of process chemicals in the equipment manufacturing/installation process.

Because process oils are used in a finite quantity in any given system, the effects described above will eventually plateau at an equilibrium level.

Figure 15 is a schematic diagram of the typical behavior of flow reduction in a capillary tube for a compressor manufactured using conventional process chemicals. The performances of the two types of commercially available POE clearly are similar. Equilibrium is typically reached after a period of 2–3 weeks.

Figure 16 shows typical results for the two main types of commercially available ester after assembly fluids and wire winding lubricants have been replaced by ester-based alternatives. The establishment of a steady state restriction is a good indication that most of the restriction occurs as a result of process chemical contamination. If lubricant hydrolysis or thermal degradation occurred to any great degree, capillary restriction would be expected to increase over time to the point of prohibitively large flow reduction (as exemplified in Fig. 16). This type of degrada-tive behavior has been observed only for lubricants that have been inappropriately formulated.

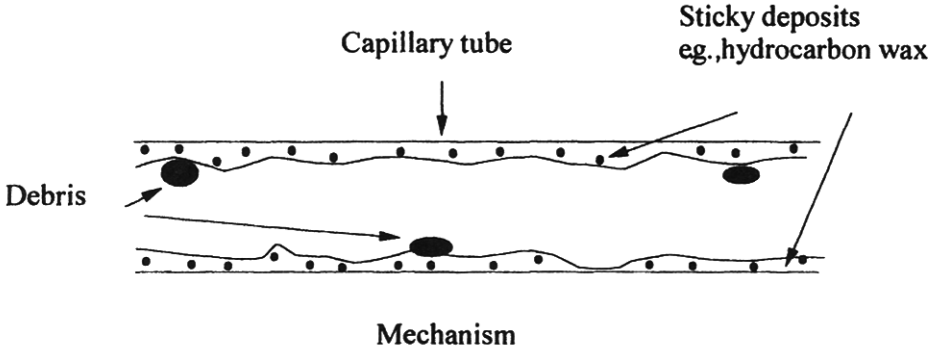


Figure 14 Schematic of deposit formation inside a capillary tube. Deposition of sticky, waxy deposits act as "fly-paper," attracting other materials, e.g., wear debris, dessicant fines, or metal sulphides.

Copyright © 1999 Marcel Dekker, Inc.

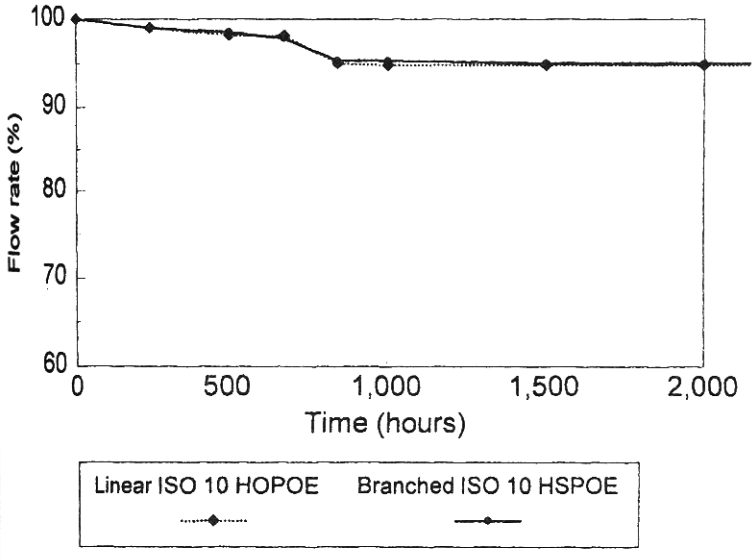


Figure 15 Typical flow reduction of ISO 10 wholly linear (HOPOE) and wholly branched (HSPOE) lubricant in a domestic appliance compressor.

Most appliance manufacturers have now introduced HFC-compatible assembly fluids, honing oils, wire winding lubricants, and so on.

Where ester based assembly fluids are used, they are typically one or two viscosity grades higher than the fill oil, to minimize drainage from the surface during assembly. The use of a higher viscosity assembly oil also provides some lubricity benefits during initial compressor break-in.

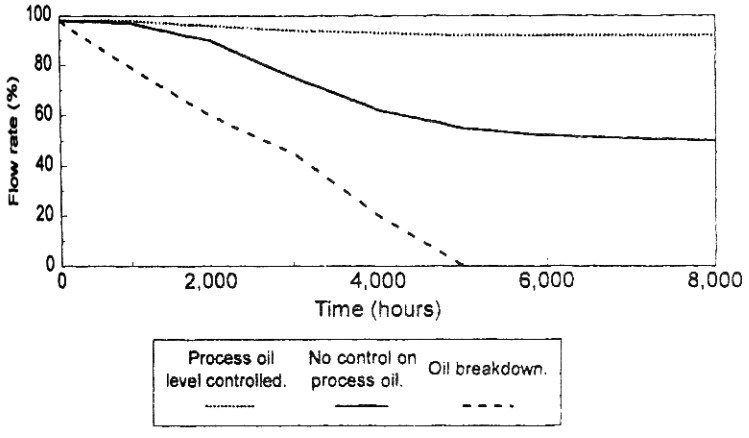


Figure 16 Plot of the effect of process oils on capillary blockage: dotted curve: assembly oil and wire lubricant replaced with ester-based alternatives, sulfur- and chlorine-containing products replaced or reduced, cleaning procedures improved; solid curve, uses same processing oils as for CFCs. Dashed curve indicates oil breakdown.

Copyright © 1999 Marcel Dekker, Inc.

Nonmetallic Components. Unlike the mineral oils they have replaced, lubricants that are compatible with HFCs tend to be polar by nature (e.g., PAGs, carbonates, esters). This increased polarity results in a tendency to swell certain types of nonmetallic (plastic or elastomeric) material.

Besides causing swelling of the material, some components within the polymer (oligomers and processing additives) are soluble in the lubricant and can be leached out. Some of the components present in many nonmetallics that can be identified in deposits in the expansion device are as follows:

processing aids (e.g., carboxylates, amines, esters)
fillers (e.g., carbonaceous compounds)
plasticizers (e.g., phthalates, diesters)
residual cross-linking compounds (e.g., sulfur-based compounds)
mold release agents (e.g., esters, hydrocarbons).

Transport of these materials to the expansion device is in the manner described above. Any particulate materials (desiccant fines, machining debris) are transported mechanically and are readily entrapped in the sticky primary deposits of organic material.

Compatibility tests have shown that in extreme cases, up to 20% by weight can be leached out of an inappropriate nonmetallic material. Table 5 summarizes the compatibility of a range of nonmetallic materials with HFC/POE refrigerant–lubricant combinations. However, it is well recognized that nominally identical materials obtained from different companies can show a large scatter in the results obtained when tested with lubricant–refrigerant mixtures. Thus, it is recommended that the specific material of interest be tested for compatibility before use in any performance-sensitive application.

Close collaboration between the compressor OEM, the lubricant supplier, and the material manufacturer can rapidly lead to solutions that minimize deposits from this source.

Lubricant Components. Poorly formulated lubricants can also produce deposits. If the ester lubricant is incorrectly formulated, components that have poor low temperature flow performance can precipitate, leading to waxy or gummy deposits and poor performance at the expansion devices. Fully branched pentaerythritol and dipentaerythritol polyol esters of certain types have very poor low temperature properties. The poor pour point of these esters can be seen in Table 6.

Industrial grades of POE with a viscosity greater than 32 cSt, if not properly formulated,

Table 5 Compatibility Summary: Nonmetallic Materials in HFC/PDE Combinations

Typically compatible[a]	Typically not compatible
Teflon (PTFE)	Butyl
Nylon 6,6	Natural rubber
HNBR[b]	Viton
Neoprene	
Buna-*N* (nitrile)	
Kalrez	

[a] Ethylene–propylene–diene monomer (EPDM) is sometimes compatible, depending on the supplier.
[b] Highly saturated nitrite butadiene rubber.

Copyright © 1999 Marcel Dekker, Inc.

Table 6 Some Fully Branched Polyol Esters Having Poor Pour Points

Ester	Pour point (°C)
ISO 32 HSPOE	−38
ISO 32 HOPOE	−48
ISO 32 linear POE	−3
ISO 46 branched POE	8
PE, branched C9 (solid)	30

can contain significant concentrations of such materials, and analysis of field units has shown that these impurities are subject to form deposits. This can happen even with lubricants that are miscible in the refrigerant to very low temperatures. Therefore, many major compressor OEMs have begun to set maximum specifications for the amount of fully branched material permissible in the lubricant.

Certain types of performance-enhancing additive can also cause problems. For example, silicone-based foaming agents have been found in expansion devices, but it is unclear whether they are a significant contributor to flow reduction. However, tests have shown that deposits of silicone-based foaming agents in the evaporator can lead to a marked drop in energy efficiency.

Inorganic Components. As described earlier, particulate debris (machining debris and desiccant fines) will adhere to the sticky organic layer laid down by the mechanism outlined in the processing oil section. Whereas a correctly formulated polyol ester will not cause copper plating, certain types of additive can have a deleterious effect and should be avoided. Residual chlorinated solvents (left over, e.g., from the degreasing processes) have been shown to be a major cause of copper plating. One possible way to avoid copper plating is to add copper deactivators (sulfur- or nitrogen-based). These additives should be used with caution, however, since they bring problems of their own and have been shown to be a major cause of deposit formation.

To avoid copper plating, it is best to avoid the use of reactive chlorinated solvents, avoid use of lubricants with high acid values, and ensure that moisture levels are adequately controlled. *Chemical and Thermal Stability of POEs. POEs* are well known to possess high thermal stability. The first large-scale commercial use of POEs was in high temperature aerospace applications, and thousands of tons per year are still in use today.

The thermal stability of a POE can be severely impaired by certain acidic species. It is therefore important that the lubricant be made to a tight acid value specification (, 0.05 mg KOH/g) and that acidic antiwear and anticorrosion additives be avoided. Certain chlorinated compounds that can also lead to a marked reduction in POE stability can be removed by proper control of process residuals.

Outside the refrigeration industry, poiyol esters are used in a wide range of applications where hydrolysis could be an issue (e.g., hydraulic fluids, air compressors). Sensible precautions are routinely taken, and hydrolysis does not cause problems. The same is also true in the refrigeration industry.

Polyol esters for the refrigeration lubricants are manufactured by reacting a polyfunctional alcohol with an organic acid with a chain length of the order of four to ten carbon atoms. The products of this reaction are the polyol ester and water. This reaction is reversible. Thus if a large amount of water is added, the ester can break down to form acids, alcohols and partial

Copyright © 1999 Marcel Dekker, Inc.

esters. This reverse reaction, known as hydrolysis, can be triggered only by the presence of high levels of moisture in combination with elevated temperatures. Below 70°C, hydrolysis is so slow as to be insignificant. If no moisture is present in the system, hydrolysis cannot occur.

Figure 17 shows how the moisture concentration in the lubricant in a hermetic appliance compressor changes with time, according to whether a drier is present. The lubricant was deliberately doped with a high level of moisture prior to the test. In the first part of the test, conducted without an in-line drier, the refrigerant purges moisture from the lubricant and the moisture content initially decreases. When an in-line drier is added to the system, the moisture level in the oil drops still further. With an in-line drier present from start-up, the equilibrium moisture content is established at a very low level, very rapidly.

Both rate and degree of hydrolysis are very dependent on moisture content. In many systems the oil is very dry (, 50 ppm) initially, and this dryness is typically further reduced by the introduction of refrigerant (, 20 ppm). With a drier present, the level of moisture is typically less than 5 ppm. At the very low levels of water generally recommended by equipment manufacturers (, 50 ppm), the degree of hydrolysis is insignificant.

Table 7 shows the analysis of oils after extended field testing in retrofit situations. Control of water and processing oils is hardest to achieve in a retrofit environment. It is clear from the data that there is little or no change in acid value. This is typical for field units. There are no examples of field failures directly attributed to hydrolysis of POE lubricants. Deposit buildup was seen, but this condition was fully attributable to processing oils. Once cleaned, no other deposits were seen.

Frequently users express the fear that hydrolysis may produce carboxylic acids, which can cause corrosion or react to form carboxylic acid salts, which can contribute to deposit formation. Carboxylic acid salts (potassium, calcium, and iron) have been detected in deposits, but it needs

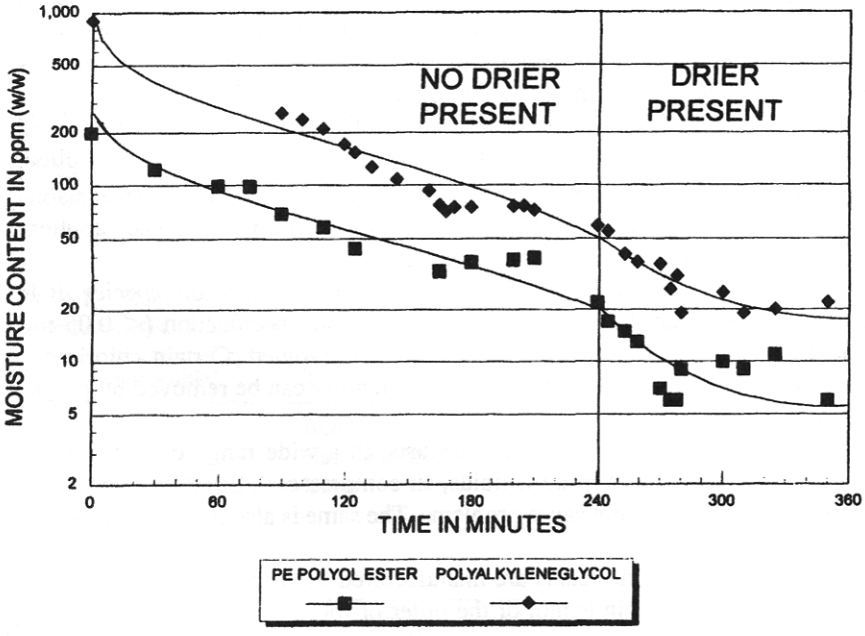


Figure 17 The effect of a drier on the moisture within a compressor.

Copyright © 1999 Marcel Dekker, Inc.

Table 7 Analysis of Oils at Four Viscosities After Extended Field Testing in Retrofit Situations

Oil viscosity at 40°C	Compressor type	Time (months)	TAN (mg KOH/g) Initial	TAN (mg KOH/g) Final	Refrigerant
32	Rotary (cap tube)	18 months	0.02	0.03	407C
68	3-Ton residential scroll (TXV)	18 months	0.02	0.02	407C
68	110-Ton Recip chiller (TXV)	18 months	0.02	0.02	407C
100	Automotive scroll (cap tube)	4 months	0.02	0.03	R134a

to be realized that carboxylates can come from a number of sources in a refrigeration system. For instance, they are used as detergents and therefore can come from process oils. They are commonly used as processing aids in elastomers, as well, and can therefore be leached out of much materials and can also be present in many brazing fluxes. Carboxylate formation is also natural consequence of the lubrication process by esters, in the absence of excessive wear and the consequential wear debris formed), however, this is unlikely to be a major source. It would be wrong therefore to assume that carboxylates found in deposits are due to the chemical instability of the polyol ester. It is possible to perform detailed chemical analysis of such carboxylates, and it is usually determined that the source is one of those described above, and is almost never due to the decomposition of the lubricant.

The organic acids typically used to manufacture refrigeration POEs are not particularly corrosive; in fact, they are stored in mild steel drums. Provided the acid value of the lubricant is kept below 0.25 mg KOH/g, and provided these acids are derived from the ester itself, there is no corrosion observed and compressor operation is not impaired.

Chemical Stability of Additives and System Extractables. Additives by their nature tend to be reactive. Antiwear additives react with metal surfaces as they grow hot as a result of friction. Copper deactivators react with copper surfaces to form an impervious layer. It is therefore not surprising that certain types of additive can have poor chemical stability. Many of the sulfur-containing antiwear additives and copper deactivators have poor chemical stability above 130°C. They can react to form sulfides with copper and iron, leading to the formation of black deposits. An example of the chemical instability of this type of additive is shown in Fig. 18, which compares flow restriction in a capillary tube with and without the additive present. Properly selected additives can help lubricant performance. As a general rule however, additives should be avoided, if possible, in refrigeration applications.

Antiwear additives and copper deactivators can also be a problem with driers containing high levels of activated alumina. Many of the antiwear additives are used to reduce alumina wear. If these additives react with alumina drier material, they may be depleted and/or form deposits.

Tribological Debris. When correctly formulated lubricants are used, metallic debris is rarely found in expansion device deposits. On the few occasions when such material has been observed, microscopic analysis has revealed that the debris is predominantly due to residual machining debris from the construction of the compressor rather than from wear.

Copyright © 1999 Marcel Dekker, Inc.

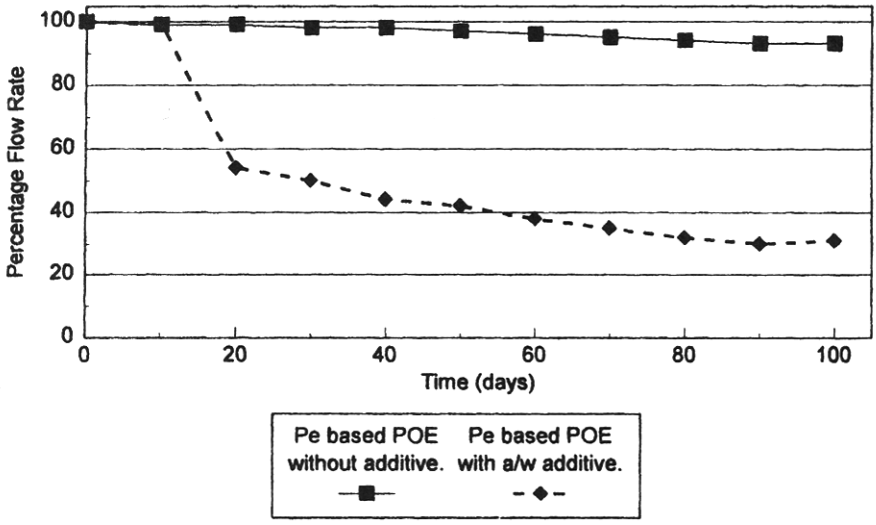


Figure 18 The effects of a poorly selected antiwear additive on capillary blockage.

It is theoretically possible that certain wear mechanisms (e.g., tribopolymerization, carboxylate formation) could contribute to deposit formation. But again, field experience has shown that these are not primary contributors to deposit formation.

Prevention. To prevent the possibility of deposit formation in expansion devices, it is necessary to thoroughly review all the materials and processing aids used in the construction of the compressor and system.

A useful first step is to prepare a flow diagram of the production process, highlighting where process chemicals are used and recording the sequence of all cleaning steps. This document can be used to identify potential problems associated with the use, for example, of materials that will not be adequately removed during cleaning. Initially, it may only be possible to assemble a list of generic descriptions or trade names of products used. A more precise chemical description of the materials being used is required, however. This often can be obtained without breaching confidentiality by examining Materials Safety Data Sheets and product specifications. More detailed information can be sought through direct dialogue with suppliers. In the past it has often proved valuable for customers and suppliers to work jointly to resolve such issues.

Table 8 lists the analytical techniques that can be used to identify any deposits found in TXVs or expansion devices. Careful sample preparation is required to avoid contamination of the deposits. These can be cross-referenced with a list of reference spectra of materials known to be problematic.

Table 9 lists basic chemical elements and compounds that have been identified as components of deposits and likely sources for such components. Contamination by small amounts of 1GS, 2GS, and 3GS mineral oil did not cause any deposit issues in expansion valves.

Conclusion. Deposits formation in capillary tubes and other expansion devices are at levels comparable with those found when CFC and mineral oil systems were used. Major OEMs have achieved this result by working closely with oil manufacturers and other suppliers to identify the problematic process chemicals and materials. Either these have been replaced by HFC/POE-compatible materials or improved cleaning processes and process controls have been introduced to limit such materials to acceptable levels.

Copyright © 1999 Marcel Dekker, Inc.

Table 8 Analytical Techniques for Identifying Deposits in TXVs or Expansion Devices

Technique[a]	Useful for determining
Optical microscopy	Physical form, morphology and distribution of phases present. Good for identifying desiccant fines, major wear debris.
Energy-dispersive x-ray (EDX)	Elemental analysis for majority of periodic table. Good first screen of nature of deposit. Good for detecting presence of inorganics.
Fourier transform infra red (FTIR)	Mainly organic analysis. Good for identifying process chemicals and nonmetallic extracts. Identifies generic classes of materials.
Mass spectrometry (MS)	
Electron impact	Good for general analysis but spectral analysis complex.
Field desorption	Softer ionization—target molecule remains intact. Good for complex mixtures.
Liquid chromatography	Highly specific analysis: discriminates between members of a generic class (e.g., carboxylates).
Tandem MS	Unique characterization of unknown molecular ions.

[a]The techniques are complementary. Used in concert, they offer a powerful tool for analysis of deposits.

4. Compressor Noise

Noise is an important aspect of a refrigerator's performance, especially in developing countries like China, where the refrigerator is kept in the living room rather than the kitchen.

Certain OEMs have found that compressors using synthetic lubricants have a noise level slightly higher than those using conventional mineral oil lubricants. Synthetic lubricants are very pure and tend not to foam. Mineral oil contains impurities, which create a degree of foaming, and the foam blanket tends to dampen the noise of a compressor. In an effort to create foam, an apparently counterintuitive approach has been tried: antifoaming agents are added at high levels (.. 1000 ppm). And indeed, foaming has been induced in synthetic lubricants by the addition of antifoaming agents at these unusually high levels.

Unfortunately, foaming agents suffer from a number of disadvantages: they are very dose rate dependent; they can lead to reductions in energy efficiency; and they can cause compatibility problems with other lubricants. Other solutions therefore must be found to address the foaming issue.

5. Energy Efficiency

Frictional energy losses due to viscous drag between the lubricant and bearing surfaces in a compressor can contribute significantly to the overall efficiency of a refrigeration system. Energy efficiency is usually expressed in terms of the coefficient of performance (COP), which is the

Copyright © 1999 Marcel Dekker, Inc.

Table 9 Chemical Deposits and Likely Sources

Chemical	Source of problem
Carboxylate (aminic or metallic)	Component of detergent used to wash metal parts
	Processing aid in elastomer
	Brazing fluxes
	Slot liners
Sulfur	Cross-linking agent in elastomers
	Additive in lubricant or processing oil (antiwear or metal deactivator)
	Porous or sintered compressor parts may have high S contamination
Zinc	Zinc diethyl dipthalate antiwear additive in honing fluid
Silicones	Foaming agent in lubricant
	Demolding agent for elastomers
	General lubricating spray used during compressor assembly
Paraffinic hydrocarbons	Wire winding lubricants
	Fin stamping lubricants
	Assembly fluids
	Greases
	Honing fluids
Borates	Fluxes
Phthalate esters	Plasticizers in elastomers

dimensionless ratio of the refrigeration effect to the heat of compression. The energy efficiency ratio (EER) is directly proportional to the COP and is expressed as follows:

EER(Btu ? W) 5 COP 3 3.412

Selection of lubricant viscosity is an important consideration in optimizing the EER. In general, the lower the lubricant viscosity, the higher the COP, hence the EER.

Test experience on HOPOEs in a number of different systems indicates that typically an increase in COP of the order of 2% can be achieved for each step to a lower viscosity grade. This is illustrated in Table 10. These figures are presented as a rough guide only and are an

Table 10 Effects on Viscosity of Increasing Coefficient of Performance (COP)

ISO grade	Percentage Increase in COP relative to an ISO 22 HOPOE
22	0
15	2
10	4
7	6

Copyright © 1999 Marcel Dekker, Inc.

approximation of the test results from several different compressors. Actual values will be dependent on the system configuration and conditions of operation. For any specific compressor design and set of manufacturing tolerances, an optimum viscosity will exist. Beyond this, piston blow by will increase, leading to a decrease in volumetric efficiency and COP. As this limit is approached, the extent of energy efficiency gains with lower viscosity will be reduced. The optimum viscosity is highly system dependent, hence very difficult to predict theoretically. Thus, direct system measurements are recommended.

Further information about energy efficiency is given in Chapter 3.

VI. CURRENT COMMERCIAL PRACTICE

A. Synthetics in Use

The refrigeration oil market consists of four main sectors:

1. Domestic appliances (household refrigerators)
2. Industrial and commercial refrigeration and air conditioning
3. Automotive air conditioning
4. After market (lubricants required for servicing existing equipment)

1. Domestic Appliances

The first sector covers the domestic refrigerator and freezer market (appliance) and has very exacting requirements for compressor lubricants. Refrigerators are designed to last 15–20 years, making system reliability of paramount importance. The compressor lubricant impacts not only compressor durability and wear but also noise, energy efficiency, and heat transfer. In the appliance sector, approvals by compressor manufacturers and cabinet manufacturers demand extensive testing. It is worth pointing out that lubricants are consumed only by the original equipment manufacturer. There is no aftermarket requirement for the appliance sector.

This sector relied heavily on CFC refrigerants and was the first area to convert to HFCs.

The approvals tests for evaluating aspects such as materials compatibility, energy efficiency, noise, and durability are exacting, and two polyol ester lubricant suppliers have emerged as industry leaders: namely ICI (HOPOEs) and Japan Energy (HSPOEs).

2. Industrial and Commercial Refrigeration and Air Conditioning

The second sector covers lubricants used in the compressors of commercial and industrial refrigeration and freezing units. Commercial refrigeration systems range from relatively small units used in store display cases to sizable systems used in manufacturing industries. Generally, smaller units relied on CFCs while the larger systems were dependent on HCFCs. This sector is currently in the process of converting to HFCs.

The industrial and commercial sector is highly fragmented. ICI, Nippon Oil, Mobil, Castrol, and Lubrizol are all major players.

3. Automotive Air Conditioning

The third sector covers lubricants used in automotive air conditioning compressors. This market traditionally used R12 as a refrigerant. In developed markets the transition to HFC has been completed.

The PAG OEM automotive air conditioning market is dominated by Apollo (Idemitsu's U.S distributor) and Union Carbide. Ester sales for the retrofit market are dominated by the same companies seen in the industrial and commercial sector.

Copyright © 1999 Marcel Dekker, Inc.

4. Aftermarket

The aftermarket covers sales of lubricants for compressor oil changes in the industrial and commercial sectors. It is estimated that when this sector is mature, it will consume four times more lubricant than is specified by the original-fill requirements of new equipment. In 1998, POEs are still in the early development stage, and currently sales to OEMs are running at around the same level as that to the aftermarket. Although original-fill lubricants are supplied directly by the lubricant supplier, the aftermarket is much more fragmented and is usually supplied by a distribution network served via a master distributor.

Existing equipment using current CFC/HCFC mineral oil technology can be easily changed over to run on an HFC/POE combination using a well-established retrofit procedure. A large retrofit subsector is therefore expected to emerge as the phaseout date of HCFCs approaches.

5. Approvals

The importance of approvals for all sectors of refrigeration and air conditioning cannot be overstated. The market structure and global nature of the refrigeration industry requires lubricants to be approved globally by all major OEMs.

A relatively small number of compressor manufacturers supply a high proportion of the global demand. It is estimated that 80% of the global compressor demand is supplied by six companies.

6. Suppliers

Two major classes of polyol esters, namely HSPOEs and HOPOEs, have attracted significant attention within the industry. European suppliers have tended to produce HOPOEs and the Japanese HSPOEs.

The market is starting to see some consolidation among suppliers, with ICI acquiring Unichema and Lubrizol purchasing CPI. Further shakeouts, or partnerships, between lubricant companies seem likely.

Table 11 presents a detailed list of the suppliers of synthetic lubricants to the refrigeration market.

B. Current Market Size

Figure 19 shows sales of global synthetic lubricants (POEs, PAGs, alkylbenzenes, etc.) to the refrigeration (CFC, HCFC, HFC, NH_3, CO_2, etc.) market.

C. Factors Affecting Incentives to Growth

The European and North American appliance markets have totally converted from R12 to alternative refrigerants. In North America and in Japan 100% usage is now with R134a. In Europe, the preferred refrigerant is also R134a. However, a minor proportion of hydrocarbon (25%) systems are also used; this is largely limited to Germany. The major drawback of hydrocarbon systems, the flammable and explosive characteristics of the refrigerant, had almost certainly ruled out their use in the United States and Japan. The proportion of R134a to hydrocarbon systems has not changed over the past few years, and a similar ratio of systems is expected to be produced in the future. Mexico will be fully converted to R134a by the end of 1998. China has produced some R134a systems recently.

Strong territorial growth is expected in China, South America, and India over the next few years.

For reasons of cost, mineral oil is still used in many HCFC industrial and commercial systems. Therefore, one of the main incentives to growth in sales of synthetic lubricants is the

Copyright © 1999 Marcel Dekker, Inc.

Table 11 Principal Suppliers of Synthetic Lubricants to the Refrigeration Industry

Supplier	Trade name	Type	Examples
ICI	Emkarate RL	POE	RL 32H
Castrol	Icematic	POE	SW 32
Mobil	Arctic	POE	EAL 32
CPI	Solest	POE	32
Lubrizol	Lubrikuhl	POE	32
DEA	Triton	POE	SE 32
ELF	Planet ELF	POE	ACD 32
Japan Energy	Freol	POE	ALPHA 32
Witco	Sun ISO	POE	SL 32
Japan Sun	Sun ISO	POE	32
Texaco	Capella	POE	HFC 32
Henkel		POE	2966A
Unichema	Priolube	POE	
Union Carbide	UCON	PAG	
Idemitsu	Daphne	PAG	
Nippon Oil		AB	
Shrieve	Zerol	AB	150
Penerco	Sontex	AB	SA 32
Soltex	Soltex	AB	AB 150

rate of phaseout of HCFCs, such as R22, in the industrial and commercial sector. Figure 20 shows the current status of this phaseout [18].

As discussed in Section IV, synthetics can also be used with different refrigerant gases (e.g., ammonia, carbon dioxide). Sales of synthetics could also be boosted by expansion into these new sectors.

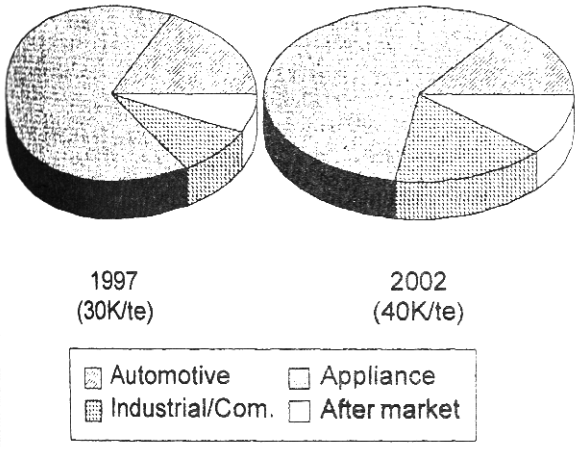


Figure 19 Sales of synthetic lubricants to the refrigeration market.

Copyright © 1999 Marcel Dekker, Inc.

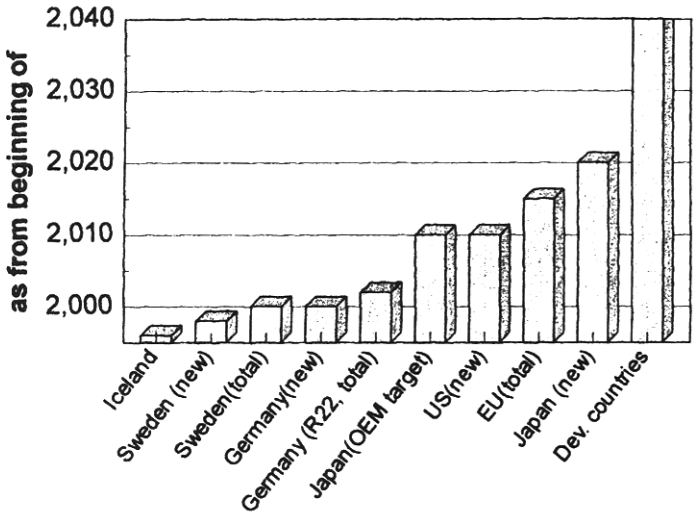


Figure 20 Phaseout of HCFCs in different countries: new, new equipment; total, total ban. (From Ref. 18.)

VII. FUTURE MARKET TRENDS

A. Market Drivers

Current market trends tend to be driven by safety, health, and environmental (SHE) issues, summarized below:

1. Compressor: scroll-and-screw compressors are increasingly used in preference to reciprocating compressors.
2. Refrigerant (which will dictate lubricant selection):
   - global warming potential (direct, and Total Environmental Warming Impact, TEWI); hydrocarbons versus HFCs.
   - flammability issues (liability issues with hydrocarbons)
   - energy efficiency
   - performance-related issues.
3. Lubricant:
   - improved energy efficiency (a trend to lower viscosities).
   - performance/cost-related issues
   - tighter SHE issues: handling, biodegradability, reuse and recycling.
   - improved lubricity: move toward SiN components in rotary compressors, increasing use of aluminum, move toward additive-free systems
   - reduced noise and vibration.

The emphasis given to each of the categories above will differ from territory to territory and from country to country depending on local policies. For example:

Improving energy efficiency has high priority in the United States because of federal mandates.
Global warming potential has a high priority in Germany and Scandinavia, being driven by strong "green" political parties.
High importance is given to tight technical specifications in Japan.

Copyright © 1999 Marcel Dekker, Inc.

B. Synthetics Under Development

Several other synthetics are currently under evaluation. These are as follows:

malanate/acrylate
ethers: polyvinyl ethers, aromatic ethers, poly(alkylene glycol) esters
carbonate esters
addivated dialkylbenzenes
modified dialkylbenzenes.

Most of these developments are driven by the need to find an HFC-compatible lubricant for use in rotary compressors. Rotaries are the most demanding of the refrigeration compressors. Current polyols are having some lubrication difficulties with systems of these types. Further developments of POE and PAG chemistry are under way to try to solve these problems. Testing of the alternative technologies is usually being carried out in parallel with POE benchmarks.

VIII. CONCLUSIONS

The refrigeration lubricant sector has been transformed by a combination of factors: legislation driven by environmental concerns, and the need for increased performance capabilities. This imposed change has led to wide-scale substitution of synthetic lubricants, principally POEs and PAGs, for mineral oil.

Prior to 1992, there were virtually no refrigeration compressors running on POEs and now there are over 250 million compressors running successfully on POEs worldwide. POEs and PAGs have become established as the lubricants of choice for the refrigeration sector, and it is likely that they will remain commercially important for the foreseeable future.

ACKNOWLEDGMENTS

I thank the technical teams at both Wilton and Runcorn, especially Andrew Whitaker and Paul Taylor, who provided data, and many of the insights, contained in this chapter.

REFERENCES

1. Nagengast, B. A. The history of refrigerants. ASHRAE paper.
2. American Society of Heating, Refrigeration, and Air Conditioning Engineers, *ASHRAE Handbook: Refrigeration Systems and Applications, SI* edition, Chapter 8, Lubricants in refrigeration systems. Printed in Mexico.
3. Sanvordenker, K. S. and Larime, M. W., A review of synthetic oils for refrigeration use, *Symposium on Lubricants, Refrigerants and Systems—Some Interactions,* ASHRAE Annual Meeting, Nassau, Bahamas, June 22–29 1972.
4. Altman, S. S., et al. Foreign Technology Division. Department of Commerce, Translation FTD-HT-23-1489-68, April 22, 1969.
5. Takeda, M., NH_3: Industrial refrigeration application, *International Symposium on HCFC Alternative Refrigerants,* paper 3.3, p. 77, the Japan Refrigeration and Air Conditioning Industry Association, Kobe, Dec, 5–6, 1996.
6. Erlangen University, Lubricants for use with carbon dioxide, *Annual Conference of German Refrigeration and Air Conditioning Association,* Hamburg, Nov. 20—21, 1997.
7. Murray, S. F., Johnson, R. L., and Swikert, M. A., Dichloromethane as a boundary lubricant for steel and other metals, *Meck Eng. 78*(3), 233 (1956).

Copyright © 1999 Marcel Dekker, Inc.

8. Komatsuzaki, S., Antiseizure and antiwear properties of lubricating oils under refrigerant gas environments, *Lubr. Engin. 47*(3), 193–198 (1991).
9. Sundaresan, S., Industry experience with HFC refrigerants—Contamination key to hermetic system integrity, *Proc. Inst. Refrig., 2*(1) (1997).
10. Sanvordenker, K., Durability of HFC-134a compressors—The role of the lubricant, *42nd Annual International Appliance Technical Conference,* University of Wisconsin, Madison, May 21–22, 1991.
11. Hilderbrand, J. H., and Scott, R. L., *Regular Solutions,* Prentice-Hall, Englewoods Cliffs, NJ, 1962.
12. Hansen, C. M., *Three dimensional solubility parameter and solvent diffusion coefficient. Importance in surface coating formulation,* doctoral dissertation, Danish Technical Press, Copenhagen, 1976.
13. Barton, A. F. M., *Handbook of Solubility Parameter and Other Cohesion Parameters,* CRC Press, Boca Raton, FL, 1985.
14. Inoue, K., and Iwamoto, A., Mutual solubility of HFC-134a and synthetic ester basestocks, *Sekiyu Gakkaishi, 35*(1) (1992).
15. Van der Waal, G. B., Properties and application of ester base fluids and PAOs, *55th Annual Meeting of the National Lubricating Grease Institute,* Wesley Chapel, FL, October 1988.
16. Johnston, U., and Hoglund, E., The influence of refrigerants on the high pressure properties of lubricating oil, Lulea University of Technology, Sweden, position paper.
17. Randles, S. J., Whittaker, A. J., Nishizawa, T., and Corr, S., Field experience with the plugging of capillary tubes and TXVs using POE lubricants, *International Conference on Ozone Protection Technologies,* Baltimore, November 1997.
18. Bunemann, T., Unichema, private communication.

Copyright © 1999 Marcel Dekker, Inc.